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(71) Applicant: **THE PROCTER & GAMBLE  
COMPANY**  
**One Procter & Gamble Plaza**  
**Cincinnati,**  
**Ohio 45202 (US)**

(72) Inventor: **Polotti, Gianmarco (NMN)**  
**Via Tonale 39**  
**I-20099 Sesto San Giovanni,**  
**Milan (IT)**  
Inventor: **Scialla, Stefano (NMN)**  
**Viale dei Caduti nella,**  
**Guerra di Liberazione, 131**  
**I-00128 Rome (IT)**  
Inventor: **Scoccianti, Raffaele (NMN)**  
**Viale Trastevere, 26**  
**I-00153 Rome (IT)**

(74) Representative: **Engisch, Gautier et al**  
**Procter & Gamble**  
**European Technical Center N.V.**  
**Temselaan 100**  
**B-1853 Strombeek-Bever (BE)**

(54) **Bleaching compositions based on benzoyl peroxide and non ionic-surfactants mixture**

(57) Bleaching compositions are disclosed which comprise a lower amount of oxygen bleach, and wherein the bleach performance at higher temperature is maintained by means of a specific surfactant system comprising a cationic surfactant and a hydrophilic nonionic surfactant.

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Technical Field

The present invention relates to bleaching compositions. The compositions herein are particularly useful for the bleaching of fabrics.

Background

Compositions for the bleaching of laundry have been extensively described in the art. Bleaching compositions can be classified into peroxide bleaching compositions and hypochlorite bleaching compositions. Peroxide bleaching compositions have the advantage over hypochlorite bleaching compositions that they are generally considered as being somewhat safer to fabrics, specifically to colored fabrics. Peroxide compositions however have the inconveniency that they are often chemically unstable, which makes it difficult to formulate peroxide bleaching compositions which are sufficiently stable to be commercialized. A possible solution to this problem consists in formulating compositions with a high level of peroxide, to extend the "effective" period of the composition. A possible drawback of this solution is that compositions may reach the user which still comprise a high amount of peroxide, whereby possible skin itching may occur if the user's skin comes in contact with the peroxide composition, before or during use. This itching phenomenon is quite moderate and fully reversible, but it does constitute potential discomfort for the user.

It is thus an object of the present invention to formulate a composition comprising a peroxygen bleach in lower amounts, i.e. in amounts where substantially no itching occurs, and which yet remain effective in bleaching fabrics.

It has now been found that this object could be met by formulating an aqueous composition comprising, in addition to lower amounts of peroxygen bleach, a water-soluble cationic surfactant in combination with a hydrophilic nonionic surfactant.

Summary of the invention

The compositions of the present invention comprise hydrogen peroxide or a source thereof, a cationic surfactant according to the formula  $R_1R_2R_3R_4N^+X^-$ , where  $R_1$  is C8-C16 alkyl or is R5-T-CO-R6, wherein T is O, NH or N-C1-C4 alkyl, R5 is a divalent C1-C3 alkylene group or  $(C_2H_4O)_m$ , wherein m is from 1 to 8, wherein each of R2,R3,R4 is independently C1-C4 alkyl or hydroxy alkyl, benzyl, or  $(C_2H_4O)_xH$  where x is from 2 to 5, not more than one of R2,R3,R4 being benzyl, and X is an anion, said composition further comprising a hydrophilic nonionic surfactant having an HLB above 13.

Detailed description of the invention

The compositions according to the present invention are peroxide bleaching compositions. Thus the compositions herein comprise hydrogen peroxide or a source thereof. As discussed hereinbefore, a problem which may occur with compositions comprising hydrogen peroxide above a certain level, is that the skin of the user which comes in contact with the composition may itch. This itching phenomenon is harmless and quickly fully reversible, but it may nevertheless cause discomfort to the user. This problem will not occur directly if the composition comprises a hydrogen peroxide source instead of hydrogen peroxide per se, but it may occur upon use, when the composition is diluted in water before use and hydrogen peroxide is then formed. The compositions herein thus comprise hydrogen peroxide or a source thereof in amounts not causing any skin itching.

Suitable sources of hydrogen peroxyde for use herein include perborates, percarbonates, persulfates and the like. It is preferred however to use hydrogen peroxide per se, and the compositions herein will comprise from 1% to 10% by weight of the total composition of hydrogen peroxide, preferably from 2% to 4%. Indeed, we have found that, when used in higher amounts, skin itching phenomenon start to appear.

Because the level of hydrogen peroxide, or source thereof, is reduced, there would result a poorer bleaching performance, compared to compositions with higher amounts of peroxygen bleach which in turn might cause skin itching. We have found that the bleaching performance at higher temperatures, e.g. as from 50 °C could be maintained, even with lower amounts of peroxygen bleach, by formulating a specific surfactant system comprising a narrowly-defined cationic surfactant as well as a narrowly-defined hydrophilic nonionic surfactant.

Accordingly, the compositions herein comprise a cationic surfactant according to the formula  $R_1R_2R_3R_4N^+X^-$ , where  $R_1$  is C8-C16 alkyl or is R5-T-CO-R6, wherein T is O, NH or N-C1-C4 alkyl, R5 is a divalent C1-C3 alkylene group or  $(C_2H_4O)_m$ , wherein m is from 1 to 8, wherein each of R2,R3,R4 is

independently C1-C4 alkyl or hydroxy alkyl, benzyl, or (C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>H where x is from 2 to 5, not more than one of R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> being benzyl, and X is an anion. It is of course possible to use herein mixtures of different cationic surfactants according to the formula hereinabove.

Preferred alkyl chain length for R<sub>1</sub> is C12-15, particularly where the alkyl group is a mixture of chain length derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohol synthesis. Preferred groups for R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are methyl and hydroxyethyl groups and suitable anion X include halide, methosulfate, acetate and phosphate ions.

Examples of suitable cationic surfactant for use herein are:

coconut trimethyl ammonium chloride, preferred for use herein, or bromide as Cequartyl ® from Rhone Poulenc and Empigen ® 5141 from Albright & Wilson,  
coconut methyl dihydroxyethyl ammonium chloride or bromide,  
decyl triethyl ammonium chloride,  
decyl dimethyl hydroxyethyl ammonium chloride or bromide,  
C12-15 dimethyl hydroxyethyl ammonium chloride or bromide,  
coconut dimethyl hydroxyethyl ammonium chloride or bromide,  
myristyl trimethyl ammonium methyl sulfate,  
lauryl dimethyl benzyl ammonium chloride or bromide as Bacforbl ® 80 from Sidobre, Sinove ® and Bardac ® 205 M from Lonza.  
lauryl dimethyl (ethenoxy)4 ammonium chloride or bromide.

The compositions herein comprise from 0.1% to 20% by weight of the total composition of said cationic surfactants, or mixtures thereof, preferably from 1% to 5%.

As a further essential ingredient, the compositions herein comprise a hydrophilic nonionic surfactant. We have found that the suitable nonionic surfactants for use herein are those having an HLB above 13. It is of course possible to use mixtures of said nonionic surfactants. A wide variety of nonionic surfactants are commercially available. Typically, nonionic surfactants are alkoxyated fatty alcohols. And the HLB of a given nonionic surfactant depends on the chain length of the fatty alcohol, the nature of the alkoxyating group as well as the degree of alkoxylation. Surfactant catalogs are available which list nonionic surfactants with their corresponding HLBs. Suitable for use herein are those which have an HLB of above 13. Such nonionic surfactants are commercially available for instance under the trade name Dobanol ®, 91-8, 91-9, 91-10 and 91-12, all from Shell.

The compositions herein should comprise from 0.1% to 20% by weight of the total composition, preferably from 2% to 10% of said hydrophilic nonionic surfactant or mixtures thereof. In a preferred embodiment of the present invention, said cationic surfactant and said hydrophilic nonionic surfactant should be present in a weight ratio of cationic to nonionic of about 1:3.

The compositions herein can be advantageously formulated as emulsions comprising two nonionic surfactants with different HLBs. Indeed, by formulating in an aqueous medium at least two different nonionic surfactants having different HLBs, a stable emulsion can be obtained. This emulsion can then be used to formulate, in a single composition, different ingredients which are otherwise poorly compatible, e.g. a bleach activator with hydrogen peroxide. In this embodiment of the invention the compositions herein comprise at least one hydrophilic nonionic surfactant, which can be the nonionic surfactant described herein before, and a more hydrophobic nonionic surfactant. Suitable hydrophobic surfactants to form the hydrophobic phase of the emulsion typically have an HLB of less than about 9. The compositions of this embodiment can be made by mixing together all the hydrophilic ingredients, i.e. water, said hydrophilic nonionic surfactant, said cationic surfactant and all other hydrophilic ingredients such as dyes, optical brighteners. Separately, all hydrophobic ingredients are mixed, i.e. said hydrophobic nonionic surfactant together with other, optional, hydrophobic ingredients which are to be formulated in the composition, such as perfumes, solvents, enzymes, bleach activators and polymers. Then, both mixtures are mixed together. If the composition comprises a bleach activator, i.e. a peracid precursor, it is preferable to choose a hydrophobic bleach activator which can be formulated in said hydrophobic mixture, and thus remains separated from the hydrophilic peroxygen bleach. This adds to the chemical stability of the compositions, thus its performance as more oxygen remains available throughout time. A suitable hydrophobic bleach activator for use herein includes acetyl triethyl citrate, as described in WO 93/12067, as well as compounds according to the formula R-O-O-R' where R and R' are independently alkyl, alkenyl, alkanoyl, aryl, aroyl, alkylaryl or alkylaroyl radicals.

We have observed that the pH of the compositions herein plays a role in the chemical stability of the composition. Accordingly, the compositions herein are preferably formulated at a pH of from 1 to 7, preferably 3 to 5. A variety of suitable means can be used for adjusting the pH of the compositions, including organic or inorganic acids, alkanolamines and the like. It may be desirable to use alkanolamines

herein, as we have found that alkanolamines have an effect on the viscosity of the product, and thus can be used as viscosity regulators, if necessary.

The compositions herein may comprise a variety of optional ingredients. A preferred optional feature of the compositions herein is the presence of radical scavengers, which are beneficial to the stability of the compositions herein. Suitable radical scavengers for use herein include the well known substituted mono and di hydroxy benzenes and their analogs, alkyl and aryl carboxylates, and mixtures thereof. Preferred radical scavengers for use herein include butyl hydroxy toluene, mono-tert-butyl hydroquinone, benzoic acid, toluic acid, t-butyl catechol, benzylamine, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, commercially available under the trade name Topanol CA ® ex ICI, as well as n-propyl-gallate. Radical scavengers, when used, are typically present herein in amounts ranging from 0.01% to 2% by weight of the total composition, preferably 0.01% to 0.2%.

The compositions herein may further comprise other optionals, including anionic and cationic surfactants, to be formulated in the hydrophilic phase herein, builders and chelants, as well as aesthetics, including dyes and perfumes and the like.

The compositions according to the present invention are useful as laundry bleaches, including for the pretreatment of stains on laundry items prior washing. Indeed, pretreatment of fabrics before washing allows a close contact of the product with the stains, and the bleaching mechanism described herein occurs at a later stage, when the pretreated fabrics are contacted with warm water. The compositions herein can also be formulated as detergent compositions per se, or as detergency additives, to be used in addition to a detergent. Compositions herein can further be used as dishwashing compositions, or as hard surface cleaners, provided that contact with warm water occurs at some point in time in the washing process.

The present invention further encompasses a process of bleaching fabrics, dishes or hard surfaces wherein said fabrics, dishes or hard surfaces are contacted with a bleaching liquor comprising a composition according to any of the preceding claims in an aqueous medium at a temperature of from 30 °C to 90 °C, and said bleaching liquor is subsequently rinsed off of said fabrics, dishes or hard surfaces. In one embodiment of this process, the composition described herein is first applied to fabrics, as a so-called pretreater, preferably to the stained portions of said fabrics, and said pretreated fabrics are subsequently contacted with an aqueous medium at a temperature of from 30 °C to 70 °C, for a period of time sufficient to bleach said fabrics. In this embodiment, said bleaching liquor is formed at the time the fabrics are introduced in said aqueous medium. Subsequently, said bleaching liquor is rinsed off of said fabrics.

The present invention is further illustrated by the following examples and data.

#### Examples - Experimental Part

The following formulations according to the present invention are made by mixing the listed ingredients in the listed proportions (in weight %).

Composition 1	
Dobanol ® 91-8	3%
Coconut trimethyl ammonium chloride	1%
H2O2	4%
Sodium Coconut Alkyl Sulfate	10%
Dobanol ® 23-3	5%
Water and minors	to balance
pH	4

Composition 2	
Dobanol ® 91-8	3%
Coconut trimethyl ammonium chloride	1%
H2O2	4%
Sodium Coconut Alkyl Sulfate	4%
Dobanol ® 23-3	10%
Water and minors	to balance
pH	4

Composition 3	
Dobanol ® 91-10	3%
Coconut trimethyl ammonium chloride	1%
H2O2	4%
Sodium Coconut Alkyl Sulfate	2%
Dobanol ® 23-3	7%
Water and minors	to balance
pH	4

Composition 4	
Dobanol 91-8	3%
Bardac ® 205M	1%
H2O2	4%
Sodium Coconut Alkyl Sulfate	2%
Dobanol ® 23-3	5%
Water and minors	to balance
pH	4

The present invention concerns the incorporation of a specific cationic/nonionic surfactant system in a liquid peroxygen bleaching composition which allows to reduce the amount of peroxygen bleach without losing performance. The technical data below illustrate the present invention. The tests are made with the following conditions. The tests are performed on cotton fabrics, with 6 replicates per test. The fabrics are stained as indicated hereinabove, and 0.2g of prototype is applied to the stains, prior to washing. Then the fabrics are washed in a Launder-O-meter, with 5 g of Dash Ultra Powder in 500 ml water. There is no waiting period between application of the prototype on the stains, and the subsequent washing.

Prototype A is a composition as composition 1 hereinabove, but without Dobanol 91-8 and without cationic surfactant. Prototype B is the same as Prototype A, but with 7% level instead of 4%. The results are listed in the table below.

Stains	Prototype 1 vs. Prototype B 40° C	Comp. 1 vs. Prototype B 40° C	Prototype A vs. Prototype B 60° C	Comp. 1 vs. Prototype B 60° C
Grass	-0.8 s	-0.2	-1.0 s	-0.3
Cocoa	+0.1	+0.3	-0.9	0.0
Tea	-0.4	-0.4	-0.7	-0.2
Wine	-0.8	-0.3	-0.7 s	0.0
Vegetal Oil	-1.0 s	+0.1	-1.0 s	0.0
Blood	-3.2 s	-1.7 s	-4.0 s	-0.8 s

The results are expressed as panel score units as evaluated by expert judges. Comparing Prototype A vs Prototype B shows that a decrease in H2O2 leads to a loss of performance. Comparing Composition 1 vs Composition B shows that Composition 1 is as good as prototype B, even though it has about half less

H2O2.

Another test is performed as in the previous experiment. In this test, composition 2 exemplified hereinbefore is compared to a reference composition. The reference is an activated bleaching composition comprising hydrogen peroxide and acetyl triethyl citrate. More specifically, the formulation comprises 6% H2O2, 3.5% acetyl triethyl citrate, 6% Lutensol ® TO3, 8% Dobanol ® 45-7, 1.5% Sodium Alkyl Sulfate, 0.3% Citric Acid, 0.2%, water to balance, pH = 4).

#### Prototype 2 vs. reference

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	40 ° C	60 ° C
Grass	+ 0.2	0.0
Cocoa	+ 0.0	+ 0.2
Tea	-0.6	-0.2
Wine	-0.1	0.0
Vegetal Oil	-0.5	-0.5
Mineral Oil	+ 0.3	+ 0.3
Make Up	+ 0.92s	+ 0.9s
Tomato	+ 0.92s	+ 0.4
Sebum	-0.67	+ 0.5
Blood	-1.0s	-4.0 s

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This comparison shows that a composition according to the present invention performs better than an activated bleaching composition comprising a higher amount of hydrogen peroxide.

#### Claims

1. A composition comprising hydrogen peroxide or a source thereof, a cationic surfactant according to the formula  $R_1R_2R_3R_4N^+X^-$ , or mixtures thereof, where  $R_1$  is C8-C16 alkyl or is R5-T-CO-R6, wherein T is O, NH or N-C1-C4 alkyl,  $R_5$  is a divalent C1-C3 alkylene group or  $(C_2H_4O)_m$ , wherein m is from 1 to 8, wherein each of  $R_2, R_3, R_4$  is independently C1-C4 alkyl or hydroxy alkyl, benzyl, or  $(C_2H_4O)_xH$  where x is from 2 to 5, not more than one of  $R_2, R_3, R_4$  being benzyl, and X is an anion, said composition further comprising a hydrophilic nonionic surfactant having an HLB above 13, or mixtures thereof.
2. A composition according to claim 1 which comprises hydrogen peroxide, in amounts of from 1 % to 10% by weight of the total composition, preferably from 2% to 4%.
3. A composition according to the preceding claims which comprises from 0.1% to 20% by weight of the total composition of said cationic surfactants, or mixtures thereof, preferably from 1% to 5%.
4. A composition according to the preceding claims wherein said cationic surfactant is coconut trimethyl ammonium chloride.
5. A composition according to the preceding claims which comprises from 0.1% to 20% by weight of the total composition of said nonionic surfactant, or mixtures thereof, preferably from 2% to 10%.
6. A composition according to the preceding claims where said cationic surfactant and said hydrophilic nonionic surfactant are present in a weight ratio of said cationic surfactant to said hydrophilic nonionic surfactant of about 1:3.
7. A composition according to any of the preceding claims which is formulated as an emulsion comprising at least two nonionic surfactants having different HLBs.
8. A composition according to any of the preceding claims which further comprises a bleach activator.

9. A process of bleaching fabrics, dishes or hard surfaces wherein said fabrics, dishes or hard surfaces are contacted with a bleaching liquor comprising a composition according to any of the preceding claims in an aqueous medium at a temperature of from 30 °C to 90 °C, and said bleaching liquor is subsequently rinsed off of said fabrics, dishes or hard surfaces.

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10. A process according to claim 9, wherein said fabrics are pretreated by applying thereon, preferably on the stained portions of said fabrics, a composition according to claims 1 to 8, and said pretreated fabrics are subsequently contacted with an aqueous medium at a temperature of from 30 °C to 70 °C, thereby forming said bleaching liquor, for a period of time sufficient to bleach said fabrics, and said  
10 bleaching liquor is subsequently rinsed off of said fabrics.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 94 87 0098

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 000 226 (PROCTER & GAMBLE CO.) * abstract * * page 7, line 32 - line 37 * * page 8, line 9 - line 10 * * page 12, line 9 - line 22 * * page 17, line 23 - line 29 * * page 19, line 27 - line 29 * ---	1,3-6,8	C11D3/39 C11D1/835
X	EP-A-0 004 121 (PROCTER & GAMBLE CO.) * page 4, line 38 - line 39 * * page 5, line 1 - line 21 * * page 20, line 6 * * claims 1-6 * ---	1,3,5-8	
X	GB-A-2 179 364 (COLGATE PALMOLIVE CO) * abstract * * page 2, line 54 - line 65 * * page 9, line 26 - line 27 * * page 10, line 31 - line 32 * * page 13, line 45 - line 65 * * page 18 - page 20; examples 3-5b * ---	1	
A	EP-A-0 012 483 (PROCTER & GAMBLE CO.) * claims * -----	1-10	
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 24 October 1994	Examiner Pelli Wablat, B
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

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